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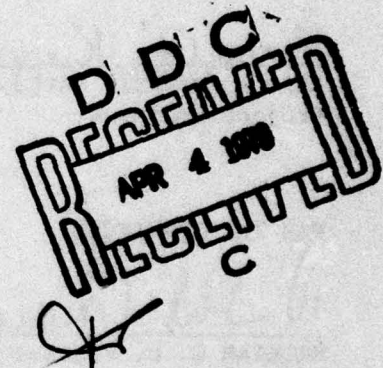
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# GENERATION OF COPPER FILMS ON LOW-EXPANSION SUBSTRATES FOR USE AS LASER MIRRORS

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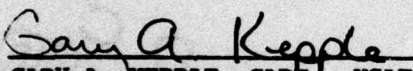WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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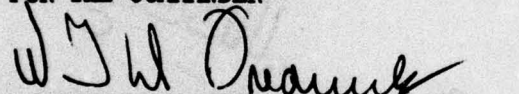
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This report deals with the feasibility of producing superior mirrors for IR laser devices by utilizing copper-coated low-expansion glass-ceramic materials. These materials are produced by a unique self-generating process. Glass-ceramics developed and evaluated in this study have exhibited highly encouraging mirror characteristics such as good film-to-substrate adhesion, high specular reflectance at ten and six-tenths micrometers and high laser damage threshold at ten and six-tenths micrometers. A total of fifty-one samples was prepared and

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evaluated for the critical substrate and copper film properties.
A total of five copper-coated samples was prepared for submittal to
AFML for further evaluations.

# PREFACE

   This report was prepared by Owens-Illinois, Inc. under contract number <u>F33615-76-C-5343</u>. The sponsoring organization was DARPA and the contract monitor was Capt. Gary Kepple of the Wright-Patterson Air Force Materials Laboratory.

   The Owens-Illinois Project Manager was Dr. N. L. Boling and the Principle Scientist was Mr. P. P. Pirooz.

   This is the final report on the project and it covers the technical effort that was conducted during the period of June 1976 to March 1977.

## TABLE OF CONTENTS

# LIST OF ILLUSTRATIONS

# LIST OF TABLES

## SUMMARY

The basic objective of this program was to determine feasibility of generating reflective copper films by diffusion on low-expansion glass-ceramic (CER-VIT) substrate materials as a technique for manufacturing laser cavity mirrors.

Although the scope of this program encompassed both materials development and product evaluation, the work was conducted on a limited scale to conform with the size of the contract.

The investigation reported herein was divided into three essential tasks:

1. Design and development of the appropriate glass-ceramic (CER-VIT) materials.

2. Optimizing and implementing the desired copper film generation technique leading to the preparation of appropriate specimens for evaluation.

3. Devising and conducting evaluation tests related to the following characteristics:

   a. Film-to-substrate adhesion
   b. Surface roughness
   c. Film thickness
   d. IR reflectance
   e. Laser damage threshold

These studies resulted in the successful development of two glass-ceramic compositions which were utilized in the preparation of the evaluation samples.

Crystallization and film generation heat-treatment methods were optimized for said compositions.

A total of seventeen copper-coated samples was evaluated for the above-mentioned properties. A significant number of the samples exhibited near 100% IR reflectance (versus silver reference) and damage threshold in excess of

the maximum output of the laser available at this laboratory ($> 6.2$ KW/cm$^2$). The film-to-substrate adhesion was rated excellent in a number of samples tested. Feasibility was demonstrated for building up the original copper film by electroplating additional metal without detrimental effects on the film properties.

# SECTION I

## INTRODUCTION

The recent increase in demand for high-power IR lasers has prompted a number of studies directed towards the advancement of the state of the art of polished metal mirrors. Yet other workers have attempted to replace the metal mirrors with alternate materials in an effort to minimize the serious thermal distorsion problem encountered by the metal mirrors subjected to high-power laser irradiation. In this vein, the purpose of the present investigation has been to evaluate copper-coated, low-expansion glass-ceramic (CER-VIT) materials as new mirror materials.

More specifically, this study was undertaken to determine feasibility of producing low-expansion glass-ceramic mirrors in which the reflective copper film is self-generated on the surface by a unique diffusion controlled process.

It was anticipated that the copper film generated by the subject process would exhibit superior film-to-substrate adhesion and laser damage threshold. This was borne out by the results obtained in a limited study which is the subject of this report.

1

## SECTION II

## BACKGROUND

The process of copper-film generation presented here is based on a phenomenon which results in the selective migration of copper ions to the glass surface by diffusion.

In a previous study, attempts were made to delineate the basic mechanism for this migration. The following discussion is based on the findings obtained from light microscopy and electron microprobe analysis of samples fired in oxidizing, reducing and neutral atmospheres.

Basically, these results have led to the conclusion that said migration is a diffusion-controlled process as indicated by the linear dependence of the depth of copper depleted layer on the square root of the heat-treatment time.

The colors produced as the result of this migration support the opinion that the migrating species are only the $Cu^+$ ions. A series of additional heat treatments have also strongly suggested that the driving force for the migration is the atmosphere in contact with the glass surface which can readily change the oxidation state of the $Cu^+$ ions. If the surface is exposed to an oxidizing atmosphere, the $Cu^+$ ions are converted to CuO which forms a continuous layer on the surface. If the immediate atmosphere is reducing, such as hydrogen, the $Cu^+$ ions will then convert to metallic copper which may again form a continuous copper film on the glass surface. In either case, the reaction depletes the surface glass of $Cu^+$ ions which are in turn replenished from the adjacent layers driven by the resultant concentration gradient. This hypothesis was verified by the heat treatment of samples in nitrogen and argon atmospheres which produced no detectable migration of the copper ions.

What is not readily explained by this hypothesis is the profile of the depleted layer. This layer appears to increase in depth as a function of the heat-treatment time and/or temperature, but, as indicated by the color change and the electron microprobe data, it does not cause a progressive change in the copper ion concentration. This suggests that each ion would be required to travel the entire depth of the depleted region after it has come under the influence of the driving force which is located at the surface. This type of mechanism is further supported by the diminishing rate of the growth of the surface layer as a function of the heat-treatment time, or the depth of the depleted layer.

It should be noted that the actual film generation behavior will also strongly depend on the host material and process parameters.

3

SECTION III

EXPERIMENTAL STUDIES

## 1.1. Preparation of the Original Glasses

The compositions of the host glasses were selected on the basis of
their ability to crystallize into a glass-ceramic body possessing a very
low coefficient of thermal expansion, near zero if possible. For this pur-
pose, two compositions were selected from totally different families of
glass-ceramics; one from the Li-Al-Si system and the other from the Zn-Al-Si
system. Both of these were expected to produce a high-quartz solid-solution
crystalline phase resulting in very low thermal expansions. To these com-
positions were added CuO at 2 and 4% levels (by weight) resulting in glasses
76184A1 and 76411A1 in the Li-Al-Si system and 76185A1-1 and 76410A1 in the
Zn-Al-Si system respectively. Glasses were prepared from these compositions
by melting a 5000 g batch in a platinum crucible heated in an electric fur-
nace for approximately 25 hours. The melting temperature for glasses 76184A1
and 76411A1 was 2600°F and that for 76185A1-1 and 76410A1 was 2900°F. All
melts were mechanically stirred using a platinum stirrer. At the completion
of the melting process, each glass was cast in a steel mold to obtain a rela-
tively large billet. In addition to the billets, several feet of cane about
0.2 inch in diameter was also obtained from each glass by directly drawing
from the molten glass. The glass billets were then annealed as contrasted
to the cane glass which was air-quenched.

## 1.2. Crystallization Studies

### 1.2.1. Heat-Treatment Results

Glass 76184A1 - the following heat-treatment information was obtained
from the temperature gradient heat treatments:

Optimum nucleation T°C =            575-600°C

Optimum nucleation time =           4-16 hours

Optimum crystallization T°C =       625-725°C

Required crystallization time: at   625°C    > 16 hrs

650°C    > 4 < 16 hrs

675°C    > 2 <  8 hrs

700°C    > 2 <  8 hrs

725°C    > 1 <  8 hrs

A substantial difference was found in the crystallization behavior between the cane samples and the cast billet samples. The cane samples more readily crystallized into low-expansion glass-ceramic bodies. For instance, when heat treated at 600°C for 4 hours plus 650°C for 16 hours, the thermal expansions were $-1.4 \times 10^{-7}$ and $8.9 \times 10^{-7}$ for the cane and billet samples respectively.

The best results for the billet samples were obtained by either an isothermal heat treatment at 625°C - 16 hours, or a two-stage heat treatment at 580°C - 16 hours plus 650°C - 4 hours, resulting in thermal expansion coefficients ranging from -1 to $-3 \times 10^{-7}$.

Temperature gradient heat treatment of a billet sample for 16 hours showed the following features: a) fracture at $\approx$ 620°C, indicating rapid transition from a high-expansion glass to a low-expansion glass-ceramic; b) a very distinct color change from light-green to a reddish-brown at $\approx$ 635°C; c) gradual fading of the reddish-brown into a light-grey starting at $\approx$ 675°C.

Thermal expansion measurements show a definite correlation between these color changes and the expansion which is determined by the preponderance of particular crystallization products. The light-green material which is caused by the excess of $Cu^{2+}$ ions, always produced a near-zero or negative expansion.

5

The red region which is expected to be rich in $Cu^+$ always produced an expansion of about $13 \times 10^{-7}$. The light-grey areas obtained at high temperatures had an expansion similar to the red region. It must be noted that said results were obtained from isothermal heat treatments. Addition of a nucleation stage to the heat treatments has a significant effect on the final results as shown by samples Nos. 6 and 21 in Table I.

As shown in Table I, the highest expansion sample was $40 \times 10^{-7}$ possessed by the original glass, and the lowest expansion value was obtained on sample No. 4 which was a cane specimen heat treated at 600°C for 4 hours plus 650°C for 8 hours.

The expansion values nearest to zero were -1.4 and $-1.1 \times 10^{-7}$ observed in the cane sample No. 5 (600°C - 4 hrs + 650°C - 16 hrs), and in the billet sample No. 20 (625°C - 16 hrs) respectively.

Glass 76411Al - the following information was obtained from the temperature gradient heat treatments performed on cane specimens.

a) Glass/crystal transition temperature for isothermal heat treatments ranging in time from 4-16 hours ranged from 620°C to 575°C respectively.

b) The optimum nucleation temperature was 580°C from a time of 16 hours.

c) The difference in the crystallization behavior between the cane and the billet samples was not as significant as was found in the case of the 76184Al glass.

The following thermal expansion data were obtained on the cane samples (Table II). The high thermal expansion of the raw glass ($49.5 \times 10^{-7}$) was lowered in a cane sample to $-1.4 \times 10^{-7}$ (sample No. 10) by an isothermal

6

heat treatment at 625°C for 16 hours. However, in the billet glass, the lowest expansion achieved was 12.3 x $10^{-7}$ (sample No. 13). The highest expansion achieved in a crystalline specimen was 17.4 x $10^{-7}$ (sample No. 5). Heat treatments at temperatures as high as 900°C did not significantly raise the expansion. This indicates that very high-expansion crystalline phases are not produced in this system within the present test conditions. This is not the case with glasses 76185Al-1 and 76410Al as will be discussed later.

Glass 76185Al-1 - temperature gradient heat treatments were conducted to study the nucleation and crystallization behavior. The following results were obtained.

a) The optimum nucleation temperature is 775°C for a 4-hour firing time.

b) Lowest crystallization temperature after 4 hours firing time was 800°C.

c) The crystalline region was opaque, but, very unexpectedly, did not generate a CuO layer up to 900°C or higher. The temperature at which the CuO generation was found appeared to be associated with a different crystalline species than that of the lower temperature region.

Thermal expansion of the material as the function of the heat-treatment cycle is presented in Table III. The low expansion of the glass (27.6 x $10^{-7}$) was further lowered to -9.1 x $10^{-7}$ in sample No. 9 when heat treated at 825°C for 16 hours, and was raised drastically to 82.1 x $10^{-7}$ in sample No. 7 by nucleating at 775°C - 4 hours and crystallizing at 900°C - 16 hours. Since the CuO generation in this glass required firing at temperatures in excess of 900°C and, on the other hand, the low-expansion materials can be produced only by heat treating below 900°C, it does not appear feasible to produce a low-expansion copper-coated glass-ceramic from this particular composition.

7

Glass 76410A1 - temperature gradient heat treatments produced the following results.

a) For a 4-hour heat treatment, the optimum nucleation temperature was 750°C.

b) As indicated by the fractures in the cane specimen, there were two drastic changes in the crystallization behavior of the glass as the function of temperature. One at $\approx$ 760°C and another at $\approx$ 890°C. The glass converted to a low-expansion body at 760°C, and to a very high-expansion body at 890°C.

In contrast to the initial glass of this type (76185A1-1), this glass did generate a CuO surface layer over the entire crystallization temperature range.

Thermal expansion data presented in Table III show a very large range of expansions depending on the heat-treatment time and temperature applied to the sample. The original expansion of the raw glass ($27.2 \times 10^{-7}$) was lowered to $3.7 \times 10^{-7}$ in sample No. 8 which was fired at 775°C for 16 hours, and raised dramatically to $111.3 \times 10^{-7}$ in sample No. 7 which was fired at 900°C for 16 hours.

It is interesting to note that the variations between the cane and the billet samples of this glass relative to their crystallization behavior were quite insignificant in contrast to the other glasses investigated here. For instance, a heat treatment at 775°C for 16 hours of samples No. 9 (cane) and No. 13 (billet) produced expansion values of $4.3 \times 10^{-7}$ and $4.4 \times 10^{-7}$.

### 1.2.2. Crystallographic Analysis

The large variations in the thermal expansion data obtained for the heat-treated samples prompted a brief study of the crystalline species present in the samples as the function of their respective heat treatments.

8

The results of these analyses are presented in Table IV. As expected, the heat-treated 76184Al sample with the negative expansion was predominantly high-quartz solid solution (HQSS). Glasses 76815Al-1 and 76410Al also showed direct correlation between the low expansion of the heat-treated sample and the predominance of HQSS phase. High thermal expansion bodies were obtained when the peak temperature of the heat treatment was > 900°C causing the predominant crystallization of gahnite ($ZnAl_2O_4$).

## 1.3. Film Generation Studies

The art of generating a copper film on the surface of these materials involves two major processes: 1) migration of the copper ions to the glass surface and their accumulation thereon, and 2) conversion of the copper oxide layers to the metallic copper.

To study these phenomena and the related process variables, flat samples approximately 4 x 4 x 0.3 cm were sawed from the glass billet. The initial studies were made with the saw-cut surface, after which surface ground and polished samples were used for the detailed property studies.

### 1.3.1. CuO Generation

There are two basic process modes for generating the CuO layer: 1) the glass is subjected to the necessary crystallization heat treatments in the form of raw stock, after which the crystallized bulk material is shaped into the desired figure and subjected to a second heat treatment to generate the CuO layer, and 2) the final figure is produced from the raw glass (non-crystalline) which will then see a combined heat treatment for bulk crystallization as well as the CuO generation.

Since a very large majority of glasses has a tendency to undergo a significant volume change (1-5%) due to crystallization which can cause disfiguring and warpage of plate samples, the first alternative discussed above is preferred and thus was used for most of the present studies.

All CuO generation heat treatments were conducted in air atmosphere. Samples were placed on a flat ceramic plate inside an electrically heated muffle furnace. The top surface of the sample was labeled so that it only would be utilized for all the subsequent tests and evaluations. This procedure was used to eliminate the effect of the setter material on the metal film as an additional parameter.

The CuO film generated on these materials was extremely hard and durable which, combined with its very strong bond to the substrate, made it difficult to remove. Hydrofluoric acid solution was found to be the only medium capable of attacking this CuO layer. However, since this acid also readily attacks the substrate material, it was not practical to make a determination of the thickness of this layer.

### 1.3.2. Copper Metal Film Generation

The generation of the metallic copper was done by the direct reduction of the CuO layer in a hydrogen-bearing atmosphere at elevated temperatures. Once the critical parameters for the CuO generation were determined and optimized, the metallizing process was controlled essentially by the following parameters: 1) firing temperature schedule, 2) firing time schedule, and 3) ambient atmosphere.

In this study the optimum conditions were determined by the study of a matrix which included a total of 21 samples. These samples, 12 mm wide, 2 mm

10

thick and varying in length, were all cut from a block of 76184Al glass previously heat treated at 600°C (4 hrs) + 650°C (32 hrs) + 700°C (32 hrs). At this point, all samples bore a surface layer of CuO.

The metal generation heat treatments were all conducted in a Lindberg muffle furnace equipped with a conveyor belt and atmosphere control provisions. The temperature profile observed by the sample as it traveled through the furnace was programmed by tuning the three independent heating zones. Figure 1 shows a typical temperature profile that was used for the majority of the samples. The residence time at the maximum temperature was determined by the speed of the conveyor belt.

The overall ranges of conditions used for said matrix studies consisted of: a) temperature: 275-540°C, b) time: 5-30 minutes, and c) atmosphere: 8-25% hydrogen mixed with nitrogen.

The primary criterion for the evaluation of these samples was film adhesion since no material was thought to be worthy of consideration for the subject application without good film-to-substrate adhesion. The detail procedure for the adhesion test is described in a separate section.

Based on the film adhesion tests, the most favorable conditions for the metal copper generation on this type of material are: a) temperature: 275-300°C, b) time: 5-10 minutes, and c) atmosphere: 8-10% $H_2/N_2$. This information was later utilized to prepare the final samples for the film property evaluations.

1.4. Film Property Evaluations

A relatively large number of samples were prepared and studied with respect to the manufacturing process variables and physical properties such as:

11

film adhesion, thickness, roughness, light reflectance and laser damage threshold.

### 1.4.1. Sample Preparation Procedure

Glass blocks approximately 35 x 35 x 25 mm were cut from the cast billet and initially heat treated in air to obtain the desired crystalline body. These blocks were then sliced with a diamond saw to obtain plates having the approximate dimensions 35 x 35 x 3 mm. This procedure was adopted in order to complete the crystallization volume adjustments prior to the desired finishing of the surface.

Once the precrystallized plates were either ground or polished, the CuO generation and the final conversion to Cu was carried out by the procedures previously described.

The various surface finishes examined here are: as saw-cut,' ground with No. 600 grit silicon carbide, ground with No. 1000 grit silicon carbide, polished with cerium oxide, and polished with diamond paste.

In the case of two samples, additional copper metal was deposited on the original film by the conventional electrolytic technique. Up to 25 $\mu$m of new metal was successfully plated on one sample. The purpose of this experiment was simply to show the feasibility of such a process.

### 1.4.2. Measurement and Test Procedures

#### a) Film adhesion test

The relative film-to-substrate adhesion was checked using the unsophisticated, but common, ''Scotch Tape Test.'' This test consisted of pressing a section of the tape (Scotch Magic Transparent Tape No. 810) on the copper film, making sure that no air remained trapped at the interface. The tape

was then peeled from the sample by pulling up slowly with a force normal to the film surface. The results were subjectively categorized as follows: excellent (no removal of the film), good (minor peeling), moderate (partial peeling with moderate force), and poor (major peeling requiring no significant force).

b) **Film thickness and surface roughness**

A Clevite Brush Surf-Analyzer 150 was used to measure the roughness of the sample surfaces and the thickness of the copper coating. This instrument drives a stylus across a horizontal surface and records the vertical motion of the stylus in microinches. It can record both profile and roughness. Roughness refers to the short-range profile, but does not record longer-range slants or undulations of the surface.

To measure the thickness of the copper coating, a small section of the copper coating was chemically removed by dipping in a solution of $FeCl_3$ for 1 minute. The Surf-Analyzer was then driven across this step to measure the thickness of the coating. Because the coating was fairly thin, only polished samples could be used for the thickness measurement. Three measurements were made on each sample.

The results of these surface roughness and profile measurements are recorded in Table V.

c) **Reflectance at 10.6 $\mu$m**

A Perkin-Elmer Model 621 Grating Infrared Spectrophotometer was used to measure the reflectance of the samples using light with wavelengths from 2.5 $\mu$m to 20 $\mu$m. The reflectance reported is relative to a silver-coated reference mirror. The absolute reflectance of this mirror is not known, but

13

is believed to be 0.98 ± 0.005. Because this instrument measures specular reflectance, only the polished samples gave meaningful results. The relative reflectances at 10.6 μm of the polished samples ranged from 101 to 90%.

The beam size was approximately 1.5 x 2 cm so many of the dark spots were included in the illuminated area. Thus, the reflectance of the clean copper areas is probably higher than the values we measured.

Most samples were measured approximately three days after their manufacture and a few days before the laser damage tests. Many samples had their reflectivity measured again about three weeks later to see if the oxidation, which was quite apparent on some samples, had lowered the reflectivity at 10.6 μm.

Table V records the reflectance data. The actual reflectance spectra are given in Figures 2 and 3.

### d) Laser damage threshold at 10.6 μm

A 70 W CW $CO_2$ laser, Coherent Radiation Model 40A, was used to irradiate the samples in five (5) second bursts. The samples were not cooled. A 25 cm focal length antireflective coated lens was used to focus the beam onto the sample. The beam diameter on the sample was determined to be approximately 1.2 mm by measuring the diameter of faint marks made on high-density alumina with a 30 W beam. Damage marks on the samples were also ≈ 1.2 mm. The samples were irradiated at nearly normal incidence, but care was taken to avoid retroreflection of the beam back into the laser. A shutter was used to limit the irradiation to 5 seconds.

The laser power was started at 10 W and increased in 10 W steps until 70 W were reached, or damage occurred. Visual observation during and after

14

the irradiation was used as the criterion for defining damage or altera-
tions to the surface. For the purposes of this report, damage means cata-
strophic damage -- the irreversible removing of the copper from the surface.
In those instances, a crater was left on the surface about 1 mm in diam-
eter and a bright flash was seen during the illumination. In other cases,
the laser irradiation had no apparent effect on the samples. The third
type of effect was a darkening or lightening of the surface, but no indi-
cation of damage.

After each exposure, the sample was translated a few mm's, so that a new
area would be irradiated by the next 5-second burst. If damage was produced
on the previous exposure, the sample was translated and the laser power was
held at the same level. If the second exposure also caused damage, the ex-
periment was stopped and that laser power was recorded as the damage thresh-
old. If the second exposure did not cause damage, the sample was again
translated and exposed to higher irradiances.

The results of the laser damage tests are recorded in Table V.

15

DISCUSSION OF RESULTS

## 2.1. Significant Problems Encountered

The following problems were encountered in the course of this program
and considered to have had a significant impact on the nature and degree
of progress made.

### a) Glass inhomogeneity

Glasses 76184A1 and 76185A1-1 to a higher degree than 76411A1 and 76410A1
were found to be relatively poor in their homogeneity. This was indicated
by the gross differences found in the crystallization behavior of the cane
samples and the billet samples. The cane samples were readily coverted
to near-zero and negative expansion materials, whereas the billet samples
remained at higher expansions when subjected to similar heat treatments.

This heterogeneity, which is believed to be for the most part variations
in the oxidation state of the ions and thermal history, was also manifested
by the nonuniform crystallization within the billet samples. The latter
caused the serious cracks which occurred in the billets due to high thermal
stresses. This problem made it necessary to heat treat relatively small
blocks of the glass for the subsequent sample preparations.

### b) Copper film discontinuities

In the majority of samples prepared from the 76184A1 and 76411A1 glasses,
the copper film exhibited circular black spots which varied widely in terms
of size and number from sample to sample, showing no clear relationship with
the heat-treatment parameters.

It is strongly felt at this time that poor homogeneity in the original
glass and presence of very small bubbles are indirectly responsible for the

undesirable blemishes. These spots are not metallic as verified by their high electrical resistivity. Use of stringent cleaning procedures prior to the film generation heat treatments did not show any effect on the nature or population of the spots, tentatively ruling out surface contamination as the primary source.

## 2.2. Characterization of the Copper Film

Table V summarizes the preparation conditions and the results of tests and measurements for all the flat plate samples made in this investigation. The three significant heat-treatment parameters tabulated are: the initial crystallization heat treatment, the CuO generation heat treatment conducted in air, and the Cu generation heat treatment performed in $H_2/N_2$ atmosphere. The surface finish shown is that of the crystallized sample prior to the CuO and Cu generation processes, with the exception of samples 40, 41, 44, 45, 46, and 47 for which the indicated surface finish is that of the raw glass. This was done so that the crystallization and CuO generation heat-treatment processes could be combined.

Samples 1 through 8 which had received no specific surface finish were evaluated only for electrical resistivity and film adhesion. These samples were used primarily to establish the sample preparation techniques.

Samples 49, 50, 53, 54, and 55 were prepared at the conclusion of the program for delivery to AFML as called for in the contract. These samples, therefore, also were not subjected to the various tests.

### a) Film adhesion

In general, film adhesion was excellent for the unpolished (ground) samples and poor for the polished samples prepared from 76184A1 and 76411A1

17

glasses. Exceptions to this generalization are samples No. 16 (76411A1 glass), No. 21 and No. 25 (76411A1 glass) which exhibited excellent adhesion. It is interesting to note that all samples prepared from glass 76410A1, whether ground or polished, showed very poor film adhesion. This glass which is from the Zn-Al-Si system does not seem to have any promise for the development of a strongly adherent film.

Preliminary studies conducted on a matrix of samples had shown that the time, temperature and atmosphere parameters of the Cu generation heat treatments are critical factors affecting the film adhesion. In general, excessive time, temperature or $H_2$ content of the atmosphere contributed to poor adhesion. The optimum conditions were found to be: 8-10 minutes, 275-300°C and 8-10% $H_2$.

b) Electrical sheet resistivity

Electrical sheet resistivity which is a measure of copper film thickness and surface purity was measured on the majority of the samples. With the exception of samples Nos. 44 through 47, the resistivity values ranged from 0.05 to 0.36 $\Omega/\square$ . The above-mentioned samples showed resistivities as high as 90 $\Omega/\square$ . These samples had all received a combined heat treatment for crystallization and CuO generation. These and other data which will be discussed later suggest that the copper film in these samples is in turn coated by an extremely thin dielectric film.

c) Surface roughness

Surface roughness of the polished glass-ceramic substrate ranged from < 200 Å to 500 Å. Samples 21 and 25 were exceptions with 2500 and 1200 Å roughness. The ground samples showed a range of 1500-1700 Å. With the exception of sample 25, the surface roughness did not change significantly with

the generation of the copper film. In sample 25, the average roughness was < 200 Å with the copper film, as compared with 1200 Å for the bare substrate. Sample 42 is a special case, in which a relatively large amount of copper was electrolitically deposited on the original copper film. The substrate surface finish was obtained from a saw cut. The plated surface was lightly polished with alumina powder and diamond paste.

### d) Film thickness

The average film thickness was determined only for the polished samples. These ranged from 0.24 to 0.51 $\mu$m. That of the copper-plated sample was 17.1 $\mu$m, most of which was due to the electroplating. Although the actual film thickness was not determined for the unpolished samples, it is also expected to be < 1 mm.

### e) Reflectance at 10.6 $\mu$m

Light reflectance was measured on ground as well as polished samples shortly after their preparation and again after about three weeks of aging. The first measurements on the polished samples resulted in 95-101% reflectance versus a silver-coated reference. That of the ground samples ranged from 54-76% apparently due to considerable scattering. It is interesting to note that the values obtained from samples 45 and 46 are extremely low, despite their bright appearance. This is believed to be further evidence for suggesting that a thin dielectric coating is present on the copper film absorbing the 10.6 $\mu$m radiation.

Although the visual appearance of the samples indicated a major discoloration due to aging, the reflectance data shown in the table do not present a clear direction. A mixed effect is shown by the data including a significant drop in three samples, a significant rise in two samples and no significant change in the remaining eight samples.

19

## f) Laser damage threshold

The damage threshold data presented in the table show a range of 2.2 $KW/cm^2$ to $> 6.2$ $KW/cm^2$. The samples with a threshold of $> 6.2$ $KW/cm^2$ displayed no sign of damage after a 5-second exposure to the maximum power output of the laser. Samples 9, 15, 17, and 24 did not damage, but displayed lightening when exposed to the laser power indicated in Table V. Although it is encouraging to have 11 samples out of a total of 14 with a damage threshold higher than the available laser power output, it leaves little that can be treated in a critical analysis.

The apparent damage morphology of these samples did not indicate any peeling or separation of the film from the glass-ceramic substrate. The failure mode appeared to be the melting of the thin copper film. The optimum film thickness will perhaps be determined by the need for adequate heat dissipation as well as good film-to-substrate adhesion.

20

SECTION V

## CONCLUSIONS

1. In a brief study, compositions from $Li_2O-Al_2O_3-SiO_2$ and $ZnO-Al_2O_3-SiO_2$ systems doped with copper at 2 to 4% levels were investigated.

2. Copper metal films were successfully generated on glass-ceramic plates exhibiting characteristics highly favorable to the laser mirror application. These included good film adhesion, high reflectance at 10.6 $\mu m$ and laser damage threshold higher than 6.2 $KW/cm^2$.

3. It was demonstrated that, if desired, the copper film can be built up by electroplating of additional metal to several micrometers without deterioration of the critical properties.

4. It is conceivable that such mirrors can be repaired by refinishing and subsequent regeneration of the copper film.

5. Extremely small thermal expansion/contraction coefficient of the substrate material will allow the utilization of very steep temperature gradients across the wall for high heat transfer rates.

6. A total of five samples was prepared for submittal to AFML for further evaluation.

SECTION VI

## Environmental Impact

**No adverse impact on the environment is anticipated from the raw materials, the finished products or the processes used in the manufacture of herein described copper-coated glass-ceramic laser mirrors.**

## TABLE I

### THERMAL EXPANSION DATA FOR GLASS 76184A1

### AS THE FUNCTION OF HEAT TREATMENT

| Sample No. | Glass No. | Sample Type | Heat Treatment | | | | $\alpha$(0-300°C) x 10$^7$ |
| | | | $T_1$-°C | $t_1$-hrs | $T_2$-°C | $t_2$-hrs | |
|---|---|---|---|---|---|---|---|
| 1 | 76184A1 | cane | -- | -- | -- | -- | 49.0 |
| 2 | '' | '' | 600 | 4 | 625 | 16 | 47.9 |
| 3 | '' | '' | 600 | 4 | 650 | 2 | 49.2 |
| 4 | '' | '' | 600 | 4 | 650 | 8 | -7.1 |
| 5 | '' | '' | 600 | 4 | 650 | 16 | -1.4 |
| 6 | '' | billet | 600 | 4 | 650 | 16 | 8.9 |
| 7 | '' | '' | 600 | 4 | 650 | 32 | 13.5 |
| 8 | '' | cane | 600 | 4 | 675 | 1 | 48.7 |
| 9 | '' | '' | 600 | 4 | 675 | 2 | -5.5 |
| 10 | '' | '' | 600 | 4 | 675 | 4 | -6.2 |
| 11 | '' | '' | 600 | 4 | 700 | 2 | -5.2 |
| 12 | '' | '' | 600 | 4 | 725 | 1 | -3.5 |
| 13 | '' | billet | 600 | 16 | 675 | 16 | 13.9 |
| 14 | '' | '' | 625 | 4 | 675 | 16 | 13.4 |
| 15 | '' | cane | 675 | 2 | -- | -- | 48.3 |
| 16 | '' | '' | 600 | 4 | 675 | 2 | -6.7 |
| 17 | '' | billet | 625 | 4 | 675 | 16 | 13.7 |
| 18 | '' | '' | 600 | 4 | 650 | 16 | 13.0 |
| 19 | '' | '' | 580 | 16 | 650 | 4 | -3.5 |
| 20 | '' | '' | 625 | 16 | -- | -- | -1.1 |
| 21 | '' | '' | 650 | 16 | -- | -- | -6.6 |
| 22 | '' | '' | 675 | 16 | -- | -- | 12.4 |
| 23 | '' | '' | 850 | 16 | -- | -- | 14.6 |

23

## TABLE II

## THERMAL EXPANSION DATA FOR GLASS 76411A1

## AS THE FUNCTION OF HEAT TREATMENT

| Sample No. | Glass No. | Sample Type | Heat Treatment | | | | $\alpha(0-300°C)$ x $10^7$ |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | | $T_1-°C$ | $t_1$-hrs | $T_2-°C$ | $t_2$-hrs | |
| 1 | 76411A1 | cane | -- | -- | -- | -- | 49.5 |
| 2 | '' | '' | 580 | 16 | -- | -- | 50.6 |
| 3 | '' | '' | 580 | 16 | 650 | 4 | 3.6 |
| 4 | '' | '' | 580 | 16 | 650 | 16 | 14.8 |
| 5 | '' | '' | 580 | 16 | 725 | 4 | 17.4 |
| 6 | '' | '' | 580 | 16 | 825 | 4 | 16.3 |
| 7 | '' | '' | 580 | 16 | 900 | 16 | 15.3 |
| 8 | '' | '' | 600 | 4 | 675 | 4 | 14.3 |
| 9 | '' | '' | 625 | 4 | -- | -- | 50.6 |
| 10 | '' | '' | 625 | 16 | -- | -- | -1.4 |
| 11 | '' | '' | 650 | 4 | -- | -- | 5.7 |
| 12 | '' | billet | -- | -- | -- | -- | 49.2 |
| 13 | '' | '' | 580 | 16 | 650 | 4 | 12.3 |
| 14 | '' | '' | 600 | 4 | 675 | 4 | 14.1 |
| 15 | '' | '' | 625 | 16 | -- | -- | 12.7 |

## TABLE III

### THERMAL EXPANSION DATA FOR GLASSES

### 76185A1-1 AND 76410A1 AS THE FUNCTION

### OF HEAT TREATMENT

| Sample No. | Glass No. | Sample Type | Heat Treatment | | | | $\alpha(0\text{-}300°C)$ x $10^7$ |
|---|---|---|---|---|---|---|---|
| | | | $T_1$-°C | $t_1$-hrs | $T_2$-°C | $t_2$-hrs | |
| 1 | 76185A1-1 | cane | -- | -- | -- | -- | 27.6 |
| 2 | '' | '' | 775 | 4 | 800 | 4 | 28.0 |
| 3 | '' | '' | 775 | 4 | 825 | 2 | 3.2 |
| 4 | '' | '' | 775 | 4 | 825 | 4 | -6.2 |
| 5 | '' | '' | 775 | 4 | 850 | 1 | -4.8 |
| 6 | '' | '' | 775 | 4 | 900 | 4 | 73.6 |
| 7 | '' | '' | 775 | 4 | 900 | 16 | 82.1 |
| 8 | '' | '' | 825 | 4 | -- | -- | 10.3 |
| 9 | '' | '' | 825 | 16 | -- | -- | -9.1 |
| 10 | '' | '' | 825 | 32 | -- | -- | -8.3 |
| 1 | 76410A1 | cane | -- | -- | -- | -- | 27.2 |
| 2 | '' | '' | 750 | 16 | -- | -- | 28.5 |
| 3 | '' | '' | 750 | 16 | 775 | 4 | 8.4 |
| 4 | '' | '' | 750 | 16 | 775 | 16 | 16.3 |
| 5 | '' | '' | 750 | 16 | 820 | 4 | 75.9 |
| 6 | '' | '' | 750 | 16 | 900 | 4 | 108.7 |
| 7 | '' | '' | 750 | 16 | 900 | 16 | 111.3 |
| 8 | '' | '' | 775 | 16 | -- | -- | 3.7 |
| 9 | '' | '' | 775 | 16 | -- | -- | 4.3 * |
| 10 | '' | '' | 800 | 16 | -- | -- | 7.4 * |
| 11 | '' | '' | 775 | 4 | 825 | 4 | 58.5 |
| 12 | '' | billet | -- | -- | -- | -- | 26.5 |
| 13 | '' | '' | 775 | 16 | -- | -- | 4.4 * |
| 14 | '' | '' | 800 | 16 | -- | -- | 6.7 * |
| 15 | '' | '' | 775 | 4 | 825 | 4 | 61.3 |
| 16 | '' | '' | 775 | 16 | -- | -- | 3.9 * |

\* Samples heated up at furnace rate from room temperature

25

## TABLE IV

## X-RAY DIFFRACTION AND EXPANSION

## OF HEAT-TREATED SAMPLES

| Glass No. | Heat Treatment °C (hrs) | $\alpha(0\text{-}300°C)$ x $10^7$ | Crystalline Phase | | |
|---|---|---|---|---|---|
| | | | Predominant | Moderate | Minor |
| 76184A1 | 600 (4) + 675 (4) | -6.2 | HQSS | -- | glass |
| 76185A1-1 | 775 (4) + 900 (16) | 82.1 | gahnite | -- | HQSS |
| 76185A1-1 | 825 (16) | -9.1 | HQSS | -- | cubic ZrO$_2$ |
| 76410A1 | 750 (16) + 775 (4) | 8.4 | HQSS ? | unidentified | ZrO$_2$ |
| 76410A1 | 750 (16 + 900 (4) | 108.7 | gahnite | -- | HQSS |

## TABLE V

### PROCESS AND PHYSICAL PROPERTIES DATA

### FOR COPPER-COATED GLASS-CERAMIC SAMPLES

| Sample No. | Glass No. | Crystal'n Heat Treatment | Surface Finish | CuO Generation °C (hrs) | Cu Generation Heat Treatment °C (min) | % H₂ | Electrical Resistivity (Ω/□) | Adhesion | % Reflectance at 10.6 μm Fresh | Aged | Roughness (Å) Substrate | Copper | Average Thickness of Copper Film (μm) | Laser damage Threshold (KW/cm²) | Sample No. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 7618A1 | II | saw cut | 625 (4) | 300 (6) | 25 | 18.0 | Pr. | ND | ND | ND | ND | ND | ND | 1 |
| 2 | " | " | " | 625 (16) | 300 (6) | 25 | 0.5 | Md. | ND | ND | ND | ND | ND | ND | 2 |
| 3 | 7641A1 | III | saw cut | 625 (4) | 300 (6) | 25 | 0.3 | Md. | ND | ND | ND | ND | ND | ND | 3 |
| 4 | " | " | " | 625 (16) | 300 (6) | 25 | 0.2 | Md. | ND | ND | ND | ND | ND | ND | 4 |
| 5 | 7618A1 | II | saw cut | 625 (4) | 300 (18) | 10 | 2.9 | Gd. | ND | ND | ND | ND | ND | ND | 5 |
| 6 | " | " | " | 625 (16) | 300 (18) | 10 | 0.6 | Gd. | ND | ND | ND | ND | ND | ND | 6 |
| 7 | 7641A1 | III | saw cut | 625 (4) | 300 (18) | 10 | 0.4 | Gd. | ND | ND | ND | ND | ND | ND | 7 |
| 8 | " | " | " | 625 (16) | 300 (18) | 10 | 0.3 | Exc. | ND | ND | ND | ND | ND | ND | 8 |
| 9 | 7618A1 | I | G (600) | 625 (16) | 275 (5) | 10 | 0.2 | Exc. | 65 | 64 | ≈ 15000 | same | ND | 4.4-6.2 (L) | 9 |
| 10 | " | " | " | 625 (32) | 275 (5) | 10 | 0.2 | Exc. | 63 | -- | ≈ 15000 | same | ND | -- | 10 |
| 11 | " | " | P (Ce) | 625 (16) | 275 (5) | 10 | 0.2 | Pr. | 100 | 102 | < 200 | same | 0.48 | > 6.2 | 11 |
| 12 | " | " | " | 625 (32) | 275 (5) | 10 | 0.2 | Pr. | 101 | 90 | ≈ 500 | same | 0.36 | > 6.2 | 12 |
| 13 | " | " | G (600) | 625 (16) | 300 (10) | 10 | 0.2 | Exc. | 63 | 62 | ≈ 15000 | same | ND | > 6.2 | 13 |
| 14 | " | " | " | 625 (32) | 300 (10) | 10 | 0.2 | Exc. | 60 | 58 | ≈ 17000 | same | ND | > 6.2 | 14 |
| 15 | " | " | P (Ce) | 625 (16) | 300 (10) | 10 | 0.2 | Pr. | 98 | 96 | < 200 | same | 0.31 | 4.4-6.2 (L) | 15 |
| 16 | " | " | " | 625 (32) | 300 (10) | 10 | 0.2 | Exc. | 100 | 100 | < 200 | same | 0.46 | > 6.2 | 16 |
| 17 | 7641A1 | I | G (600) | 625 (16) | 275 (6) | 10 | 0.2 | Exc. | 67 | 72 | ≈ 15000 | same | ND | 3.5-6.2 (L) | 17 |
| 18 | " | " | " | 625 (32) | 275 (6) | 10 | 0.3 | Exc. | 54 | 64 | ≈ 15000 | same | ND | 4.4 | 18 |
| 19 | " | " | " | 625 (16) | 275 (7) | 10 | ND | Exc. | ND | ND | ND | ND | ND | ND | 19 |

27

TABLE V - CONTINUED

| Sample No. | Glass No. | Crystal'n Heat Treatment | Surface Finish | CuO Generation °C (hrs) | Heat Treatment °C(hrs) | % H₂ | Electrical Resistivity (Ω/□) | Adhesion | Reflectance at 10.6 μm Fresh | Aged | Roughness (Å) Substrate | Copper | Average Thickness of Copper Film (μm) | Laser damage Threshold (KW/cm²) | Sample No. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 20 | 76A11A1 | I | G (600) | 625 (32) | 275 (7) | 10 | 0.2 | Exc. | ND | ND | ND | ND | ND | ND | 20 |
| 21 | " | " | P (Ce) | 625 (16) | 275 (6) | 10 | 0.3 | Exc. | 90 | 86 | ≈ 2500 | same | ND | 2.2 | 21 |
| 22 | " | " | " | 625 (16) | 275 (7) | 10 | 0.4 | Exc. | ND | ND | ND | ND | ND | ND | 22 |
| 23 | " | " | G (600) | 625 (16) | 300 (10) | 10 | 0.1 | Exc. | 76 | 76 | ≈ 15000 | same | ND | > 6.2 | 23 |
| 24 | " | " | " | 625 (32) | 300 (10) | 10 | ND | Exc. | 72 | 62 | ≈ 15000 | same | ND | 4.4-6.2 (L) | 24 |
| 25 | " | " | P (Ce) | 625 (16) | 300 (10) | 10 | 0.2 | Exc. | 95 | 94 | ≈ 1200 | < 200 | 0.24 | 3.5 | 25 |
| 26 | " | " | saw cut | 625 (16) | 274 (6) | 10 | 0.25 | Exc. | ND | ND | ND | ND | ND | ND | 26 |
| 27 | " | " | " | 625 (32) | 275 (6) | 10 | 0.20 | Exc. | ND | ND | ND | ND | ND | ND | 27 |
| 28 | " | " | " | 625 (16) | 275 (6) | 10 | 0.10 | Exc. | ND | ND | ND | ND | ND | ND | 28 |
| 29 | " | " | " | 625 (32) | 275 (6) | 10 | 0.10 | Exc. | ND | ND | ND | ND | ND | ND | 29 |
| 30 | 76L8A1 | I | P (Ce) | 625 (16) | 275 (6) * | 11 | 0.20 | Pr. | ND | ND | ND | ND | ND | ND | 30 |
| 31 | " | " | " | 625 (32) | 275 (6) * | 10 | 0.15 | Pr. | ND | ND | ND | ND | ND | ND | 31 |
| 32 | " | " | G (600) | 625 (16) | 275 (6) * | 10 | 0.20 | Pr. | ND | ND | ND | ND | ND | ND | 32 |
| 33 | " | " | " | 625 (32) | 275 (6) * | 10 | 0.25 | Pr. | ND | ND | ND | ND | ND | ND | 33 |
| 34 | " | " | saw cut | 625 (16) | 275 (6) * | 10 | 0.25 | Pr. | ND | ND | ND | ND | ND | ND | 34 |
| 35 | " | " | " | 625 (32) | 275 (6) * | 10 | 0.25 | Pr. | ND | ND | ND | ND | ND | ND | 35 |
| 36 | 76A10A1 | IV | G (600) | 750 (16) | 300 (5) | 10 | 0.40 | Pr. | ND | ND | ND | ND | ND | ND | 36 |
| 37 | " | " | P (Ce) | 750 (16) | 300 (5) | 10 | 0.30 | Pr. | ND | ND | ND | ND | ND | ND | 37 |
| 38 | " | " | G (600) | 750 (32) | 300 (5) | 10 | 0.30 | Pr. | ND | ND | ND | ND | ND | ND | 38 |
| 39 | " | " | P (Ce) | 750 (32) | 300 (5) | 10 | 0.20 | Pr. | ND | ND | ND | ND | ND | ND | 39 |
| 40 | 76A11A1 | V | saw cut | V | 300 (5) | 10 | 2.0 | Exc. | ND | ND | ND | ND | ND | ND | 40 |
| 41 | " | " | " | V | 300 (16) | 10 | 2.0 | Exc. | ND | -- | ≈ 3000 | ≈ 1000 | 17.1 | ND | 41 |
| 42 | " | I | " | 650 (32) | 300 (16) | 10 † | 0.05 | Md. | ND | | | | | | > 6.2 | 42 |

28

TABLE V - CONTINUED

| Sample No. | Glass No. | Crystal'n Heat Treatment | Surface Finish | CuO Generation °C (hrs) | Heat Treatment °C(min) %H₂ | | Electrical Resistivity (Ω/□) | Adhesion | Reflectance at 10.6 μm Fresh | Aged | Roughness (Å) Substrate | Copper | Average Thickness of Copper Film (μm) | Laser damage Threshold (Kv/cm²) | Sample No. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 43 | 76-11-A1 | I | saw cut | 650 (64) | 300 (16) | 10 | † 0.05 | Pr. | ND | -- | ND | ND | ND | ND | 43 |
| 44 | " | V | G (600) | V | 275 (6) | 10 | ∞ | Exc. | ND | -- | ND | ND | ND | ND | 44 |
| 45 | " | " | G (1000) | V | 275 (6) | 10 | 3.0 | Exc. | 0 | -- | ND | ND | ND | 2.6 | 45 |
| 46 | " | " | P (Ce) | V | 275 (6) | 10 | 2.0 | Gd. | 13 | -- | ND | ND | ND | 5.3 | 46 |
| 47 | 76-10-A1 | VI | saw cut | VI | 275 (6) | 10 | ∞ | Pr. | ND | ND | ND | ND | ND | ND | 47 |
| 48 | 76-8-A1 | II | G (1000) | 625 (32) | 300 (10) | 10 | 0.25 | ND | ND | ND | ND | ND | ND | ND | 48 |
| 49 | " | " | P (Ce) | 625 (32) | 300 (10) | 10 | 0.15 | ND | ND | ND | ND | ND | ND | ND | 49 |
| 50 | " | " | P (D) | 625 (32) | 300 (10) | 10 | 0.15 | ND | ND | ND | ND | ND | ND | ND | 50 |
| 51 | " | I | G (1000) | 625 (32) | 300 (10) | 10 | 0.20 | ND | ND | ND | ND | ND | ND | ND | 51 |
| 52 | " | " | " | 625 (32) | 300 (10) | 10 | 0.20 | ND | ND | ND | ND | ND | ND | ND | 52 |
| 53 | " | " | " | 625 (32) | 300 (10) | 10 | 0.20 | ND | ND | ND | ND | ND | ND | ND | 53 |
| 54 | " | " | P (Ce) | 625 (32) | 300 (10) | 10 | 0.15 | ND | ND | ND | ND | ND | ND | ND | 54 |
| 55 | " | " | P (D) | 625 (32) | 300 (10) | 10 | 0.15 | ND | ND | ND | ND | ND | ND | ND | 55 |

Legends: Heat-treatment schedules:
I = 60°C/hr → 580°C (16) + 30°C/hr → 650°C (4) + 30°C/hr → 650°C (0) + F.R. → R.T.
II = 110°C/hr → 600°C (4) + 110°C/hr → 650°C (16) + F.R. → R.T.
III = F.R. → 580°C (16) + F.R. → 650°C (4) + F.R. → R.T.
IV = F.R. → 775°C (16) + F.R. → R.T.
V = F.R. → 625°C (16) + F.R. → R.T.
VI = F.R. → 750°C (16) + F.R. → R.T.

G (600) = Ground with No. 600 silicon carbide grinding powder
G (1000) = Ground with No. 1000 silicon carbide grinding powder
P (Ce) = Polished with cerium oxide grinding powder
P (D) = Polished with diamond paste
Pr. = Poor
Md. = Moderate
Gd. = Good
Exc. = Excellent
ND = Not determined
(L) = Lightening

* = Received six repeated firings
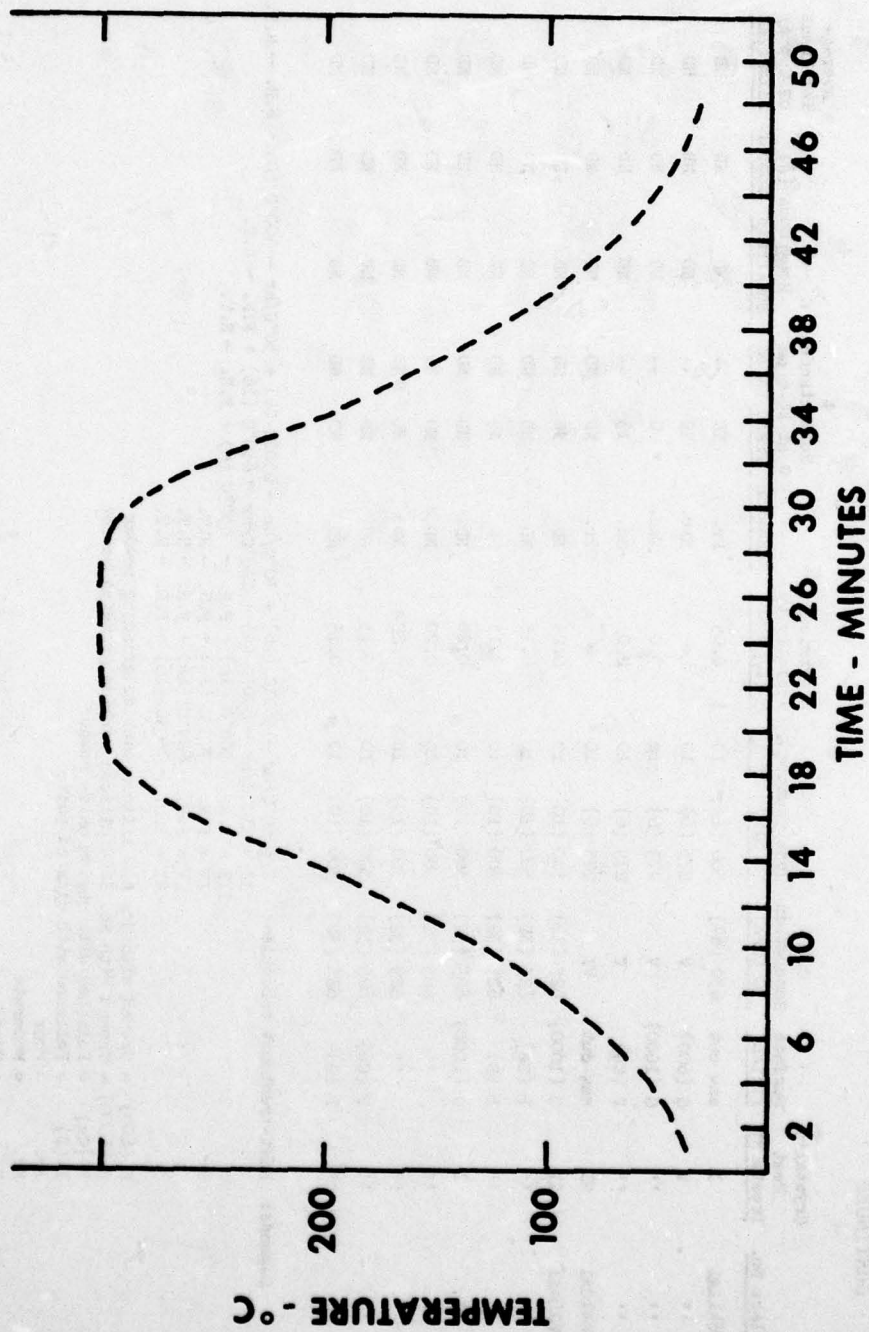† = New copper was electrolytically deposited on the original film

29

Figure 1

FIRING CYCLE FOR COPPER FILM GENERATION
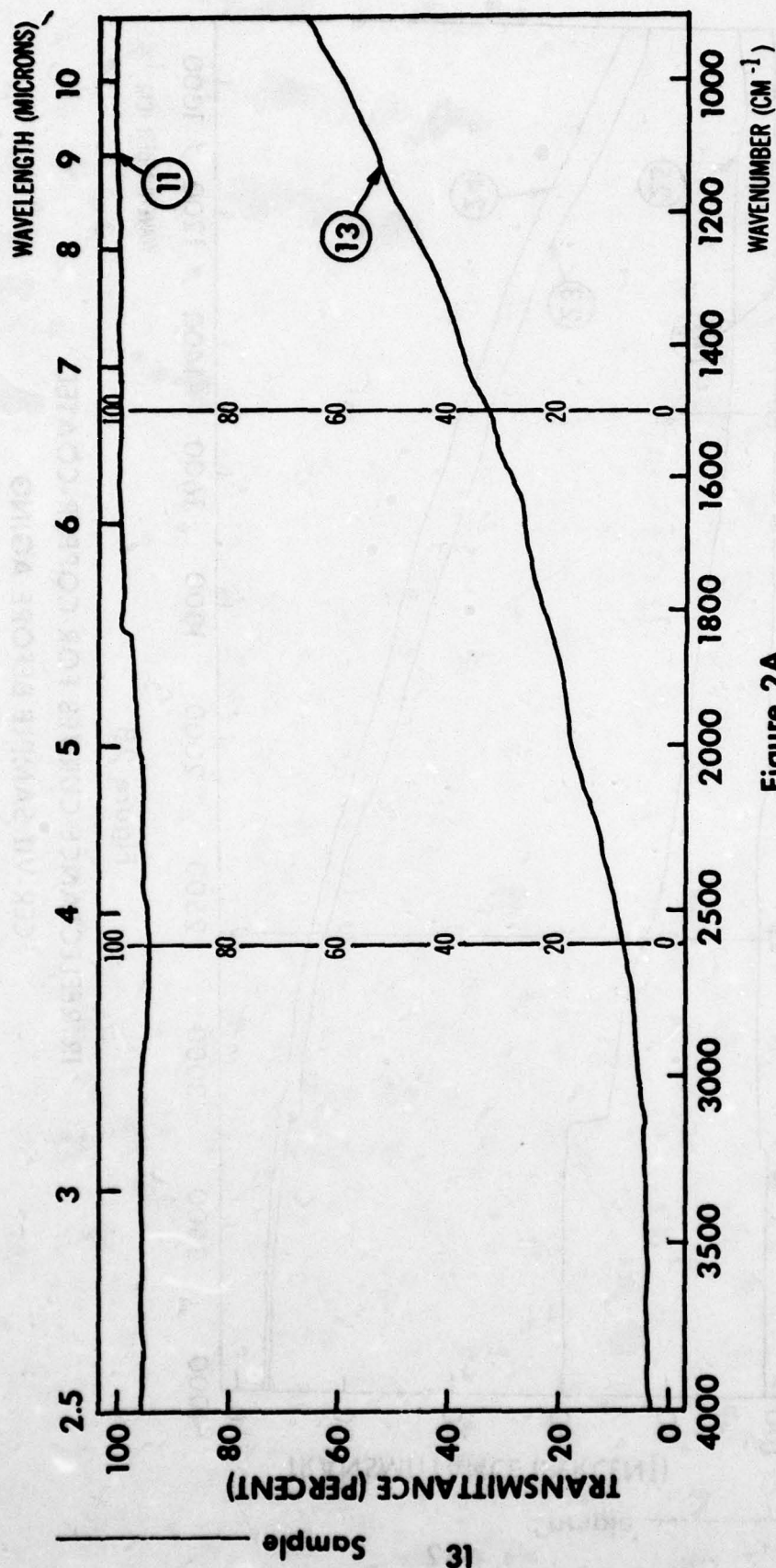
TIME – MINUTES

TEMPERATURE – °C

30

Figure 2A

IR REFLECTANCE CURVES FOR COPPER-COATED
CER-VIT SAMPLE BEFORE AGING
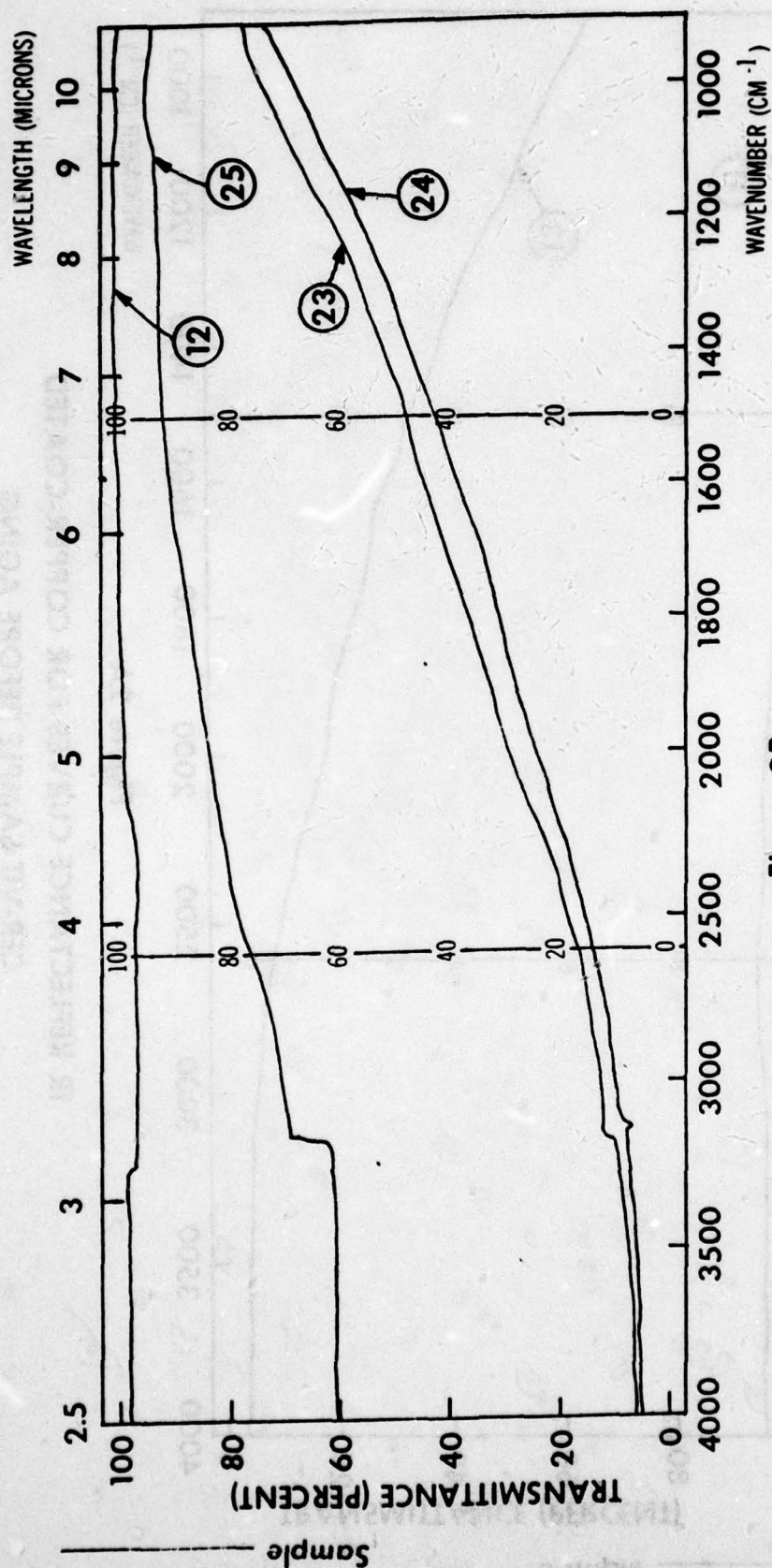
Figure 2B

IR REFLECTANCE CURVES FOR COPPER-COATED
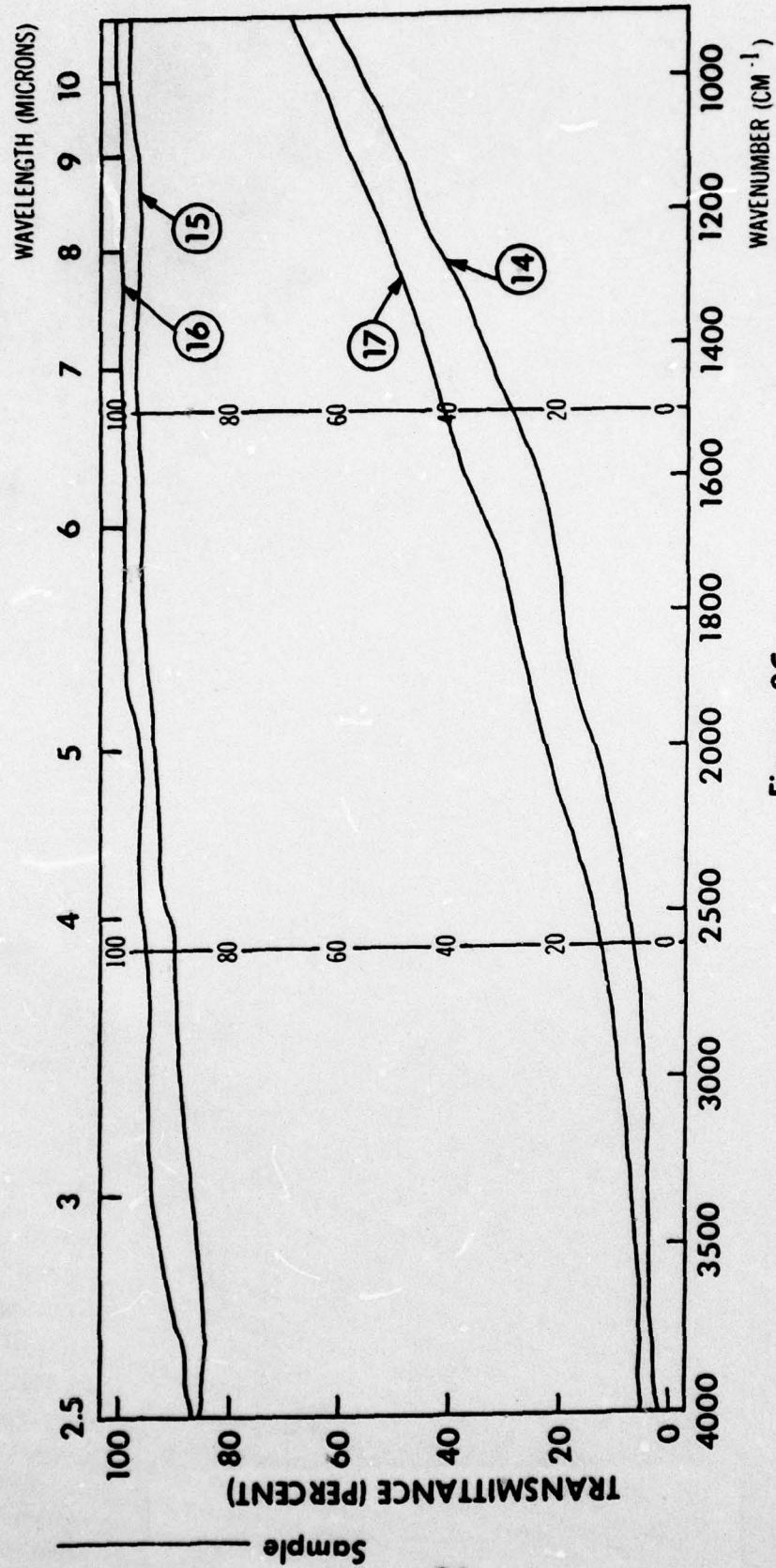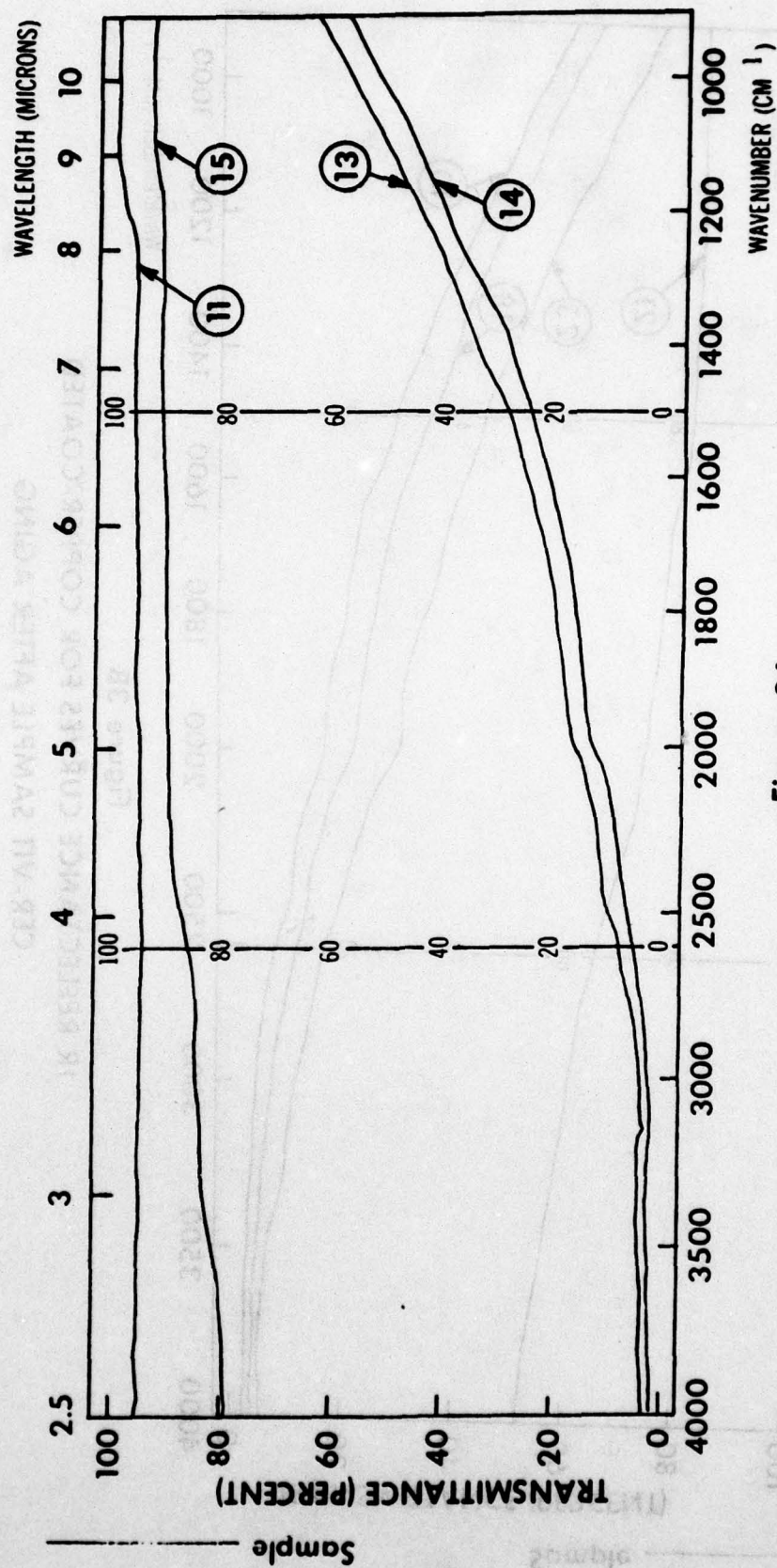CER-VIT SAMPLE BEFORE AGING

Sample

32
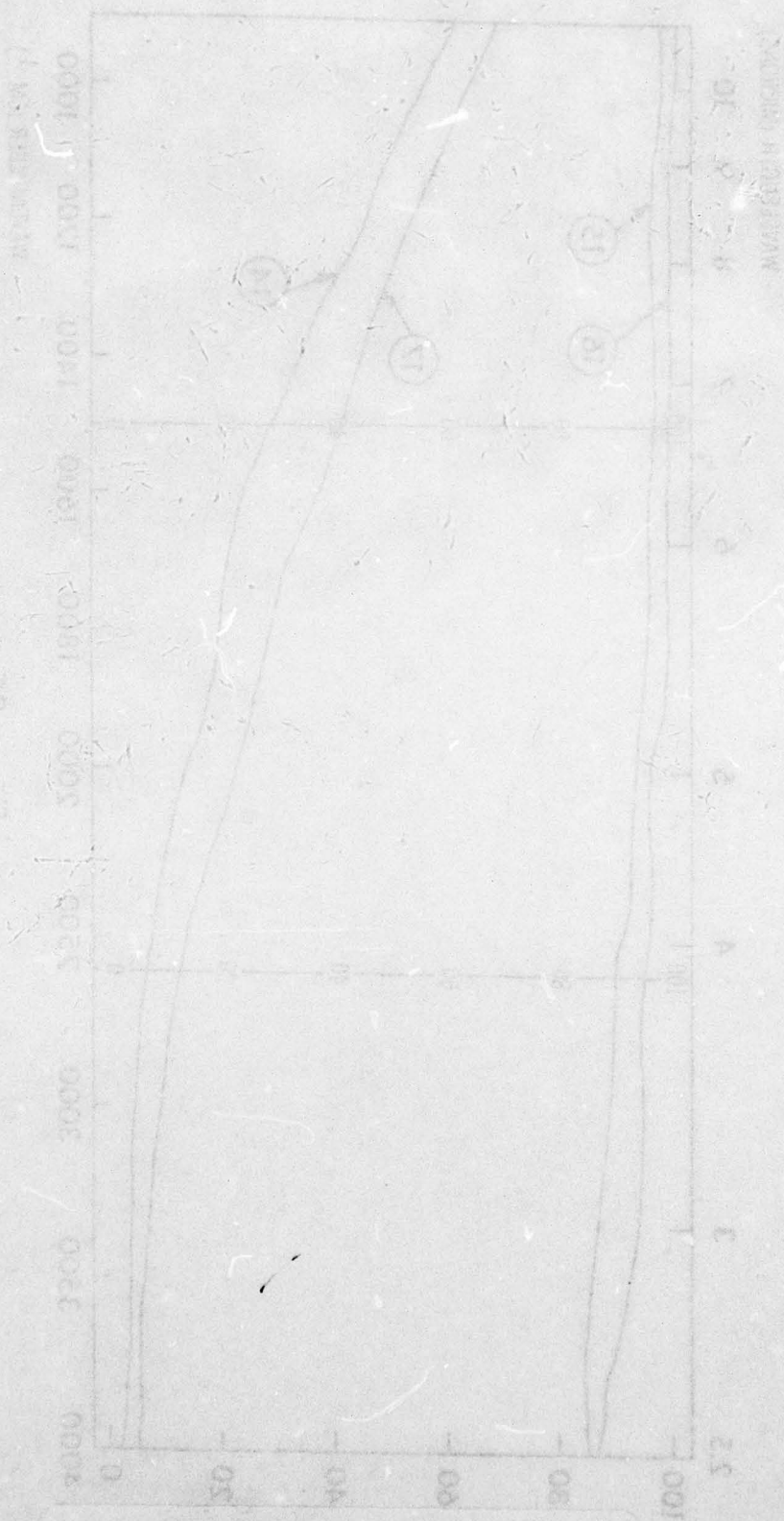
Figure 2C

IR REFLECTANCE CURVES FOR COPPER-COATED
CER-VIT SAMPLE BEFORE AGING

34

Figure 3A

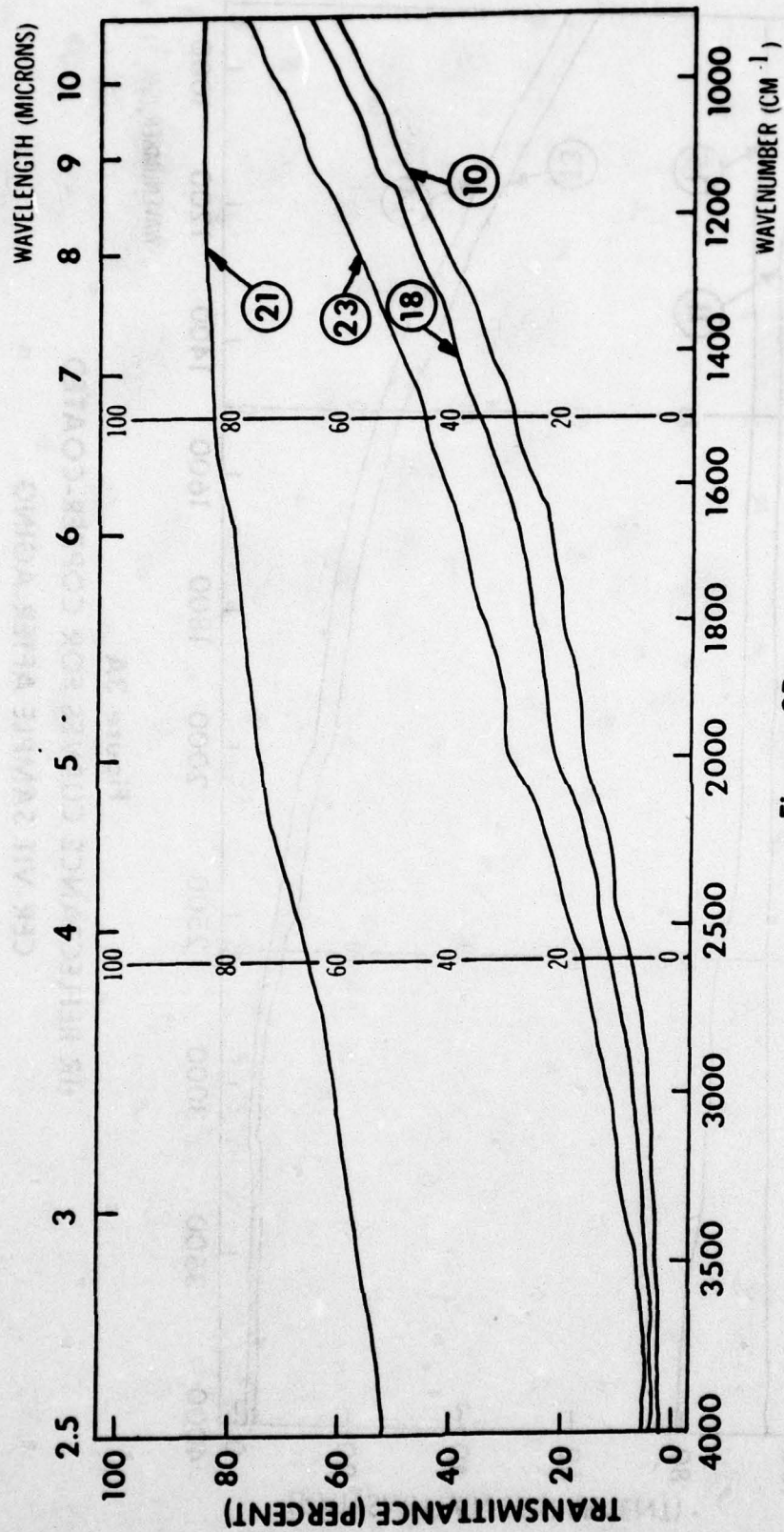IR REFLECTANCE CURVES FOR COPPER-COATED
CER-VIT SAMPLE AFTER AGING

35

Figure 3B

IR REFLECTANCE CURVES FOR COPPER-COATED
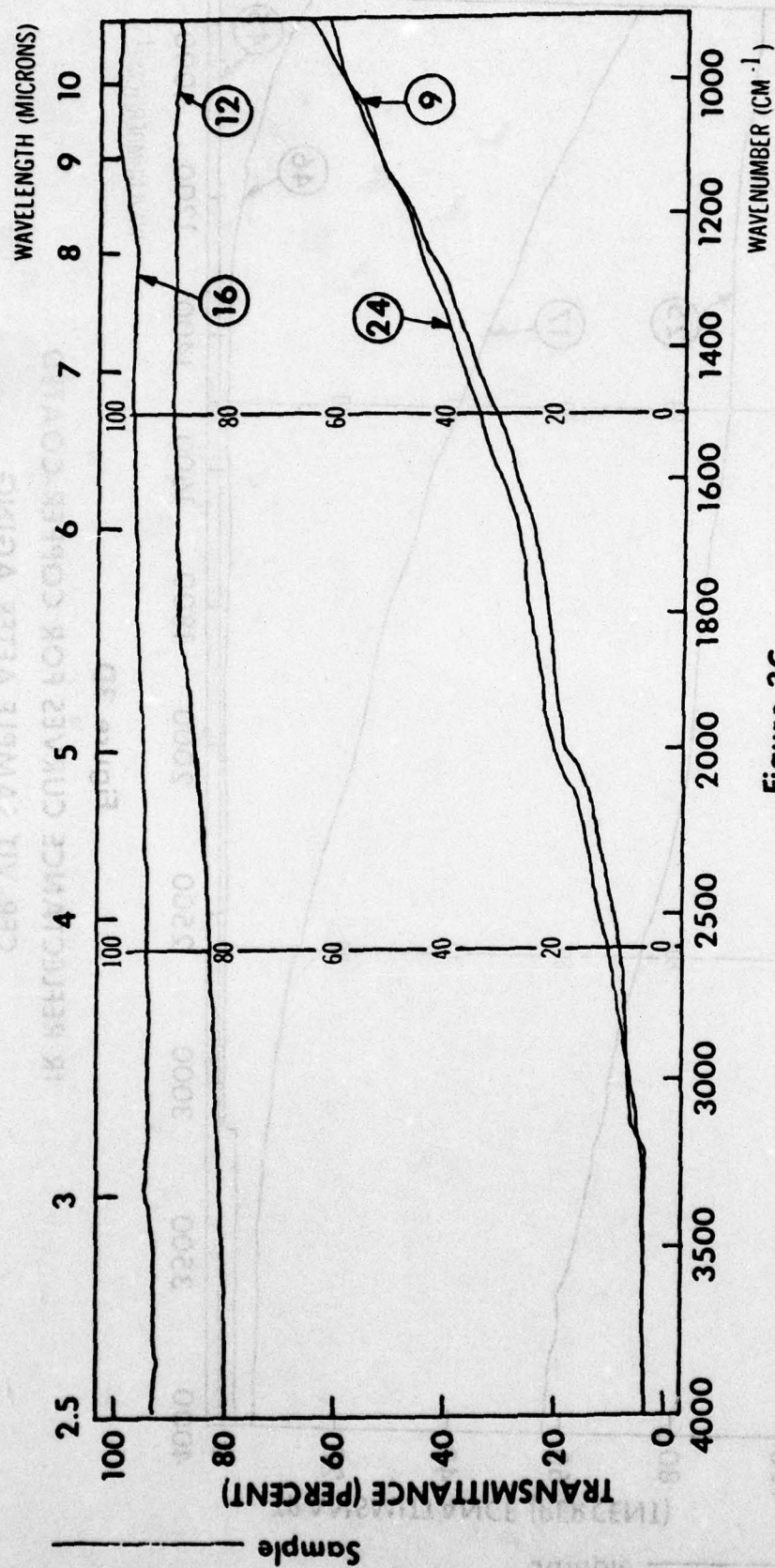CER-VIT SAMPLE AFTER AGING

Figure 3C

IR REFLECTANCE CURVES FOR COPPER-COATED
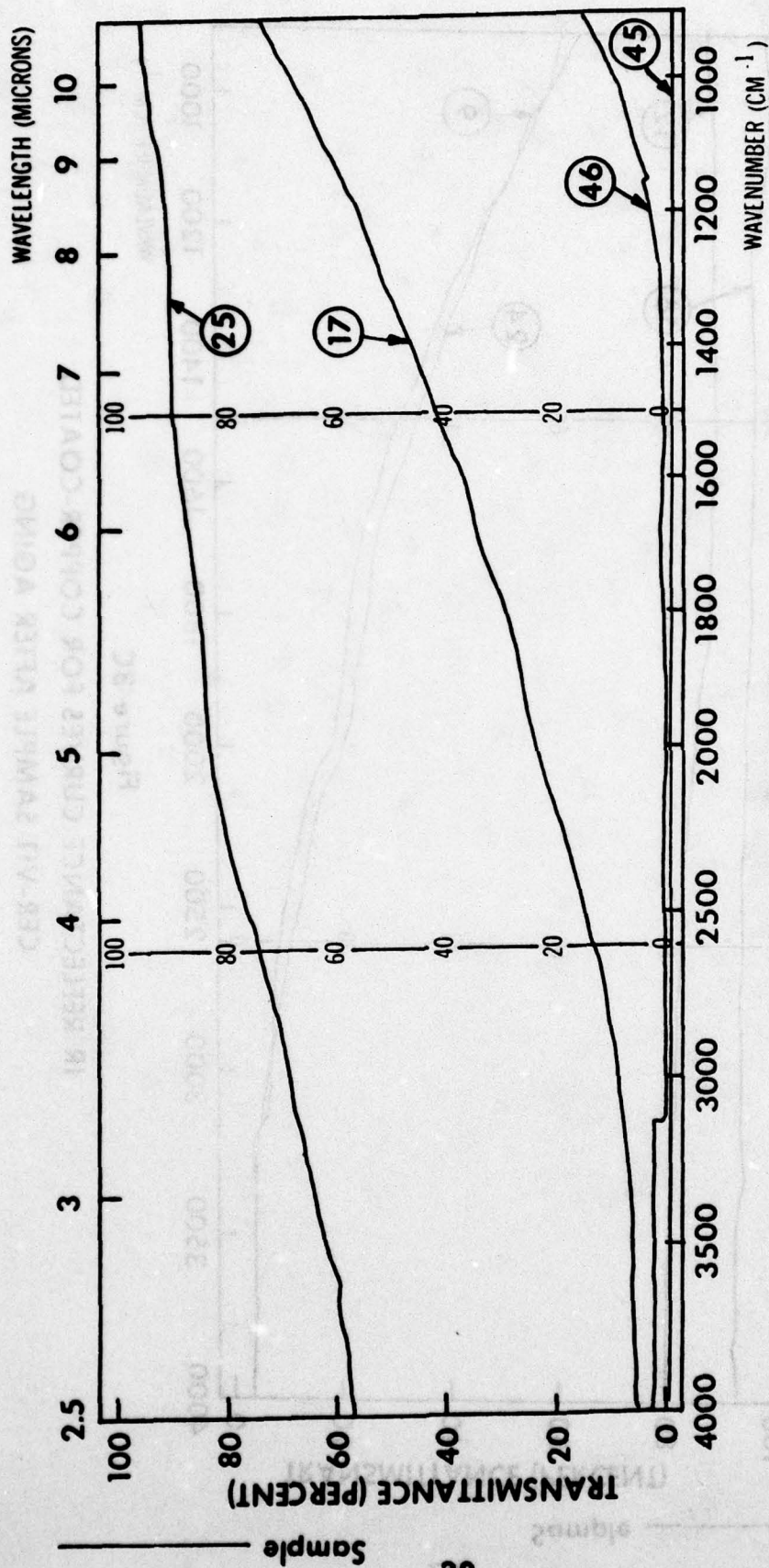CER-VIT SAMPLE AFTER AGING

Figure 3D

IR REFLECTANCE CURVES FOR COPPER-COATED
CER-VIT SAMPLE AFTER AGING

38